

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

Treatment of the exchange interactions in Hartree-Fock LCAO calculations of periodic systems

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/104166> since

Published version:

DOI:10.1021/j100315a010

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

Treatment of the Exchange Interactions in Hartree-Fock Linear Combination of Atomic Orbital Calculations of Periodic Systems

M. Causà, R. Dovesi, R. Orlando, C. Pisani,*

Institute of Theoretical Chemistry, University of Turin, via P. Giura 5, I-10125 Torino, Italy

and V. R. Saunders

Daresbury Laboratory, Science and Engineering Research Council, Daresbury, Warrington, WA44AD, United Kingdom (Received: April 2, 1987)

The range of exchange interactions in realistic HF computations for solids is discussed. Results are reported for graphite, hexagonal boron nitride, *all-trans*-polyacetylenes, lithium, and silicon. It is shown that for insulators the convergence of the series is very rapid; for silicon, for example, the inclusion of the second (sixth) neighbors in the summation reduces the total energy error to 1×10^{-3} (5×10^{-5}) au per cell. In the case of zero gap or metallic systems, long-range interactions are shown to give nonnegligible contributions to the total energy of the system (terms involving distances of 40 au can be as large as 1×10^{-6} au per cell in graphite) but do not appreciably affect the wave function of the system.

I. Introduction

The nonlocal exchange term in the Hartree-Fock (HF) Hamiltonian is believed to represent the bottleneck preventing an extensive use of this approach in solid-state physics; with respect to this problem, the introduction of correlation corrections is considered to be a relatively easy task.¹ As a matter of fact, the implementation of efficient truncation criteria of the exchange series is of primary importance; otherwise, the number of two-electron integrals that are to be calculated and manipulated may become enormous and may represent the rate-determining step in crystalline calculations. This problem has been therefore the object of careful investigation in recent years.²⁻⁴

When a representative set of atomic orbitals (AO) is adopted, the exchange contribution to the crystal energy per unit cell can be written as follows⁵

$$E^{\text{ex}} = -(1/4) \sum_{g,l,1,2,3,4} P_{ij}^g P_{kl}^g \sum_m (\chi_l^0 \chi_3^m | \chi_j^1 \chi_4^{1+m}) \quad (1)$$

where χ_j^l is the j th AO in the crystal cell identified by the direct lattice vector \mathbf{g} (0 labels the reference zero cell), and $(abcd)$ represents as usual the bielectronic integral involving the overlap distributions ab and cd . P_{ij}^g is the element of the density matrix referring to the AO's χ_i and χ_j , and is obtained by summing over the manifold of the occupied crystalline orbitals $|a_l(\mathbf{k})\rangle$ (l being the band index, \mathbf{k} the wave vector index, and $\epsilon_l(\mathbf{k})$ the corresponding eigenvalue) the product of the coefficients of the involved AO's:

$$P_{ij}^g = 2 \sum_l \int_{\text{BZ}} a_{il}^*(\mathbf{k}) a_{jl}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{g}) \theta[\epsilon_F - \epsilon_l(\mathbf{k})] d\mathbf{k} \quad (2)$$

The integral is extended to the Brillouin zone (BZ), and the step function θ annihilates the integrand if the eigenvalue $\epsilon_l(\mathbf{k})$ is above the Fermi energy ϵ_F .

In eq 1, the sum over \mathbf{m} can be limited to the first few terms because the two-electron integral decays exponentially with \mathbf{m} . The infinite sums over the lattice vectors \mathbf{g} and \mathbf{l} can be limited to within a spherical region of radius R^{ex} , corresponding to the range of the exchange interaction. R^{ex} can loosely be defined as the shortest distance such that all P_{ij}^g elements are negligible when

referring to two AO's χ_i^0 and χ_j^1 separated by a distance larger than R^{ex} . In some cases the exchange range is, however, quite large so that this "distance-only" truncation criterion (same for all ij couples) can be not very effective. A detailed study of the long-range behavior of the \mathbf{P} matrix in one-dimensional periodic systems has been effected by Kertész et al.^{2,3} with reference to an infinite chain comprising two AO's per unit cell. In the conducting case (nonalternant polymer), the \mathbf{P} matrix elements were found to asymptotically exhibit $1/r$ decay, a result well-known for this kind of systems;^{6,7} for insulators, long-range exponential decay was observed, with the decay constant critically dependent on the ratio between the interband gap and the bandwidth of the occupied band. These results were essentially independent of the kind of Hamiltonian used, either a model extended Hückel, or an ab initio HF one. Quite similar conclusions were independently reached by Piela et al.⁴ in their HF study of periodic chains of hydrogen atoms.

Information of comparable detail is lacking in the case of two- and three-dimensional periodic systems. Elementary considerations⁷ suggest that a similar distinction applies in those cases between insulators and conductors, as far as the asymptotic trend of \mathbf{P} matrix elements is concerned. In the presence of a free-electron-like conduction band, the long-range behavior of \mathbf{P} is nearly independent from the crystalline structure and is mainly determined by the discontinuity in the integrand function of eq 2 across the Fermi surface. Apart from an oscillating factor, the asymptotic decay rate of \mathbf{P} follows a $1/r^d$ law, d being the dimensionality of the system. In insulators, all bands are either vacant or fully occupied, and no Fermi surface exists. In the simplest case where an occupied band is associated with a specific, exponentially decaying AO (χ_u , say), the contribution of that band to \mathbf{P} is simply the inverse of the overlap submatrix associated with the χ_u AO's on the crystal atoms; the range of \mathbf{P} is then strictly dependent on crystal structure and orbital size, but its asymptotic decay rate must be exponential. This classification is important in principle but is of scarce practical relevance. Real systems may bear little resemblance with these extreme situations, and exhibit intermediate behavior within the range which is of interest from the point of view of the numerical convergence of the results.

As will be documented in the following, for many systems, both conductors and semiconductors, the exchange range may encompass a large number of direct lattice vectors.

In such cases, the associated problem arises of the accurate evaluation of P_{ij}^g elements referring to large $|\mathbf{g}|$ values, which

(1) Von der Linden, W.; Fulde, P.; Bohnen, K. P. *Phys. Rev. B* **1986**, *34*, 1064.

(2) Monkhorst, H. J.; Kertész, M. *Phys. Rev. B* **1981**, *24*, 3015.

(3) Surjan, P. R.; Kertész, M.; Karpfen, A.; Köller, J. *Phys. Rev. B* **1983**, *27*, 7583.

(4) Piela, L.; André, J. M.; Fripiat, J. G.; Delhalle, J. *Chem. Phys. Lett.* **1981**, *77*, 143.

(5) Pisani, C.; Dovesi, R. *Int. J. Quantum Chem.* **1980**, *17*, 501.

(6) Ukrainskii, I. I. *Theor. Chim. Acta* **1975**, *38*, 139.

(7) Economou, A. N. *Green's Functions in Quantum Physics*; Springer Verlag: Berlin, 1979.

TABLE I: Systems Considered in This Work^a

system	basis set	$n_k(N_k)$
all-trans-polyacetylene		
alternant (insulator)	STO-3G	24 (48)
symmetric (conductor)	STO-3G	24 (48)
graphite monolayer	STO-2G	61 (576)
hexagonal BN monolayer	STO-2G	109 (576)
lithium	minimal (see text)	72 (1728)
silicon	STO-2G	72 (1728)

^a n_k is the number of \mathbf{k} sampling points in the irreducible part of the Brillouin zone, where the Fock equations have been solved; N_k is the corresponding number of points in the full Brillouin zone.

requires performing an integral over the Brillouin zone, involving strongly oscillating integrand functions. In practice, the integral is performed on the knowledge of eigenvectors and eigenvalues at a selected number of sampling \mathbf{k} points. Using a simple cubature formula for calculating $\mathbf{P}^{\mathbf{k}}$ up to infinite distance leads to a nonphysical divergence of the exchange contribution.⁸ This problem is particularly evident when the large unit cell (LUC) approach⁹ is adopted for the solution of the periodic problem, since then the Fock equations are solved at a single point ($\mathbf{k} = 0$) of the reduced Brillouin zone. For ensuring the correct asymptotic behavior of the $\mathbf{P}^{\mathbf{k}}$ matrix, some authors have proposed "modulating functions" of finite range that correct the \mathbf{P} matrix as calculated by the simple cubature formula.^{8,10-12} In the present work this problem has been bypassed by considering a sufficiently dense net of sampling \mathbf{k} points, such that the \mathbf{P} matrix is correctly described within the exchange sphere.

One of the purposes of this paper is to provide for the first time a rather detailed documentation of the importance of long-range exchange contributions in realistic HF multiband calculations of crystals. The systems considered here (the graphite and hexagonal boron nitride monolayer, polyacetylene, lithium, and silicon) cover a wide range of cases, both regarding their dimensionality and their chemical characteristics. The documentation collected here shows the feasibility of a flexible criterion for truncating the exchange series, which takes into account the different ranges of the various terms that enter in a given calculation.

II. Computational Details

All computations reported here were performed using CRYSTAL, an ab initio HF program for periodic systems.^{5,13} Table I lists the systems considered in the present work, the adopted basis sets, and the number of sampling \mathbf{k} points. The STO- n G basis functions are the Gaussian-type AO's described by Hehre et al.¹⁴ The minimal basis set used for lithium comprises two s-type AO's per atom, the core one consisting of six contracted Gaussians as employed in previous work,¹⁵ and the valence one of a single Gaussian with exponent coefficient 0.2 au. The experimental geometries were employed where available; for polyacetylenes, the C-C bond lengths were taken to be 1.37 and 1.41 Å in the alternant structure, and 1.39 Å in the symmetric (metallic) structure, while the C-C-C bond angle was fixed at 124° in both cases.¹⁶

The main parameters that will be discussed in the following are the values of individual elements of the \mathbf{P} matrix, and total

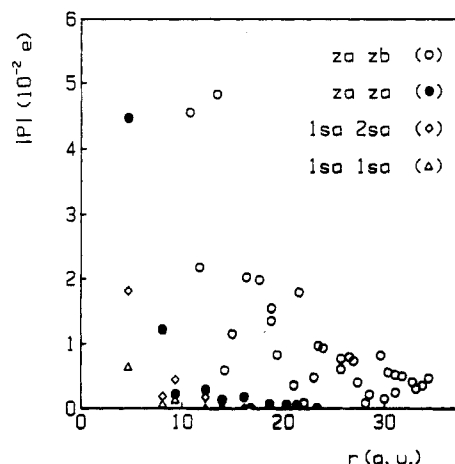


Figure 1. Absolute value of four kind of \mathbf{P} matrix elements ($P^{\mathbf{k}}_{\mu\nu}$) for the graphite monolayer, as a function of the distance r between the centers of the involved AO's χ^0_μ and χ^0_ν . The various symbols refer to different matrix elements as specified in the inset. a and b refer to the two atoms in the unit cell; $z \equiv p_z$.

energy data. The latter refer to the high-precision limit, that is, to the result obtained with a cutoff radius R^{ex} such that the sum of the excluded contributions is less than 10^{-5} au per cell. The $\mathbf{P}^{\mathbf{k}}$ matrix elements of interest are evaluated by using an integration technique previously described;¹⁷ the number of sampling \mathbf{k} points will be indicated in each case.

The influence of exchange terms on the calculated crystal energy is estimated according to one of two possible criteria:

(a) after obtaining the \mathbf{P} matrix from a high-precision self-consistent calculation, different truncations of the sums indicated in eq 1 are considered, corresponding to different values of the cutoff exchange radius;

(b) different self-consistent calculations are performed by including specified subsets of exchange integrals; the truncation of the exchange series, in this case, not only affects the exchange energy, but also the kinetic and Coulomb terms, since the wave function is changed to some extent with respect to the high-precision limit.

III. Range and Relevance of Exchange Contributions

We shall discuss first the case of the graphite monolayer for which the range and importance of exchange contributions have been analyzed most carefully.

Figure 1 shows the value of different types of \mathbf{P} matrix elements as a function of the distance r between the involved AO's. Since the graphite monolayer comprises two atoms per unit cell, the AO's are identified by specifying not only their quantum number, 1s, 2s, x , y , z , (x , y , z standing for $2p_x$, $2p_y$, $2p_z$), but also the atom, a or b, to which they belong. As expected, core-core elements such as $P^{\mathbf{k}}_{1s_a 1s_a}$ decay most rapidly with distance; yet, their value is nonnegligible up to a distance of a few angstroms, although core bands of graphite lie deep in energy and are quite flat. This happens because 1s functions contribute appreciably to crystalline orbitals of the valence band, due to the constraint of the latter to be orthogonal to core bands. For the same reason, the core-valence elements $P^{\mathbf{k}}_{1s_a 2s_a}$ are appreciably long ranged. Among all valence \mathbf{P} elements, those involving p_z orbitals are prevailing at large distances. This is not surprising if one considers that the corresponding valence and conduction bands are the widest ones and that they touch each other at the extreme of the Brillouin zone.¹⁸ Of the two types of $P^{\mathbf{k}}_{zz}$ terms, the one referring to translationally inequivalent atoms ($P^{\mathbf{k}}_{2s_a 2p_z}$) appears to be by far the more important for large $|\mathbf{g}|$ values. This behavior is similar and

(8) Evarestov, R. A.; Lovchikov, V. A.; Tupitsin, I. I. *Phys. Status Solidi B* **1983**, *117*, 417.

(9) Dobrotvorsky, A. M.; Evarestov, R. A. *Phys. Status Solidi B* **1974**, *66*, 83. Evarestov, R. A. *Phys. Status Solidi B* **1975**, *72*, 569. Evarestov, R. A.; Lovchikov, V. A. *Phys. Status Solidi B* **1977**, *79*, 743.

(10) Evarestov, R. A. *Sov. Phys.-Solid State (Engl. Transl.)* **1985**, *27*, 847.

(11) Smith, P. V.; Szymanski, J. E. *Vacuum* **1983**, *33*, 625.

(12) Smith, P. V.; Szymanski, J. E.; Matthew, J. A. D. *J. Phys. C* **1985**, *18*, 3157.

(13) Dovesi, R.; Pisani, C.; Roetti, C.; Saunders, V. R. *Phys. Rev. B* **1983**, *28*, 5781.

(14) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(15) Dovesi, R.; Ferrero, E.; Pisani, C.; Roetti, C. *Z. Phys. B* **1983**, *51*, 195.

(16) Dovesi, R. *Int. J. Quantum Chem* **1984**, *26*, 197.

(17) Angonoa, G.; Dovesi, R.; Pisani, C.; Roetti, C. *Phys. Status Solidi B* **1984**, *122*, 211.

(18) Dovesi, R.; Pisani, C.; Roetti, C. *Int. J. Quantum Chem.* **1980**, *17*, 517.

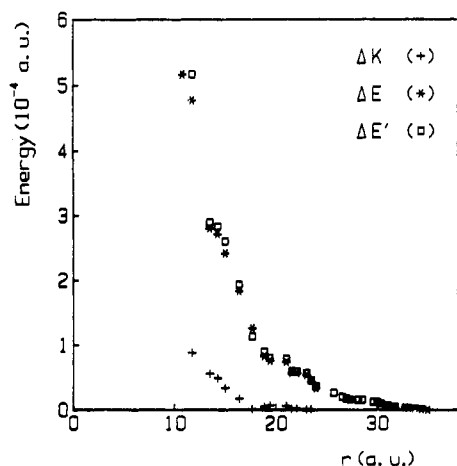


Figure 2. Energy convergence properties of the graphite monolayer. ΔE and ΔK are the difference of total and kinetic energy with respect to the limiting value when the calculation is performed by neglecting all terms involving P_{zazb}^g elements beyond a distance r . $\Delta E'$ is the difference of total energy with respect to the limiting value calculated in the same way as ΔE , but using the \mathbf{P} matrix resulting from a high-precision calculation. For other explanations, see text.

has the same origin as that observed for P_{ab}^g elements in conducting model polymers.²

It may be of interest to check to what extent the behavior of \mathbf{P}^g elements is related to overlap effects; it is in fact well-known that in the case of no variational freedom \mathbf{P} reduces to twice the inverse overlap matrix $(\mathbf{S}^{-1})^g$. In the present case this is true, roughly speaking, for the core-core and core-valence elements whereas the P_{zazb}^g elements have a much longer range than the corresponding $(\mathbf{S}^{-1})^g$ elements.

The present data, referring to a minimal basis set, are not altered in any essential way when a split valence basis is employed. In particular, the behavior of P_{zazb}^g is very similar to the one shown in Figure 1.

Consider now the effect of long-range exchange contributions on total energy and wave function. Figure 2 reports results obtained for the graphite monolayer with an STO-2G basis set. The differences of total (ΔE) and kinetic (ΔK) energy with respect to the high-precision limit were obtained following the criterion b discussed in the previous section; that is, a number of independent calculations were performed, where all nonnegligible exchange contributions were retained except for those associated with $p(g) = P_{\text{zazb}}^g$ factors, which were neglected beyond a certain distance between the two centers. It is seen that the convergence of total energy toward the limiting value closely follows the pattern of the $p(g)$ terms reported in Figure 1: a cutoff radius r of 20 au is needed, corresponding to $|p(g)| \approx 10^{-2}$ for total energy to approach the limiting value to within 10^{-4} au. On the other hand, the convergence of kinetic energy is much faster. This seems to indicate that long-range exchange contributions do not affect appreciably the wave function, which is in fact confirmed by the $\Delta E'$ data also reported in Figure 2, and obtained according to criterion a. The fact that ΔE and $\Delta E'$ are very close to each other beyond a few angstroms shows that long-range exchange interactions act rather as a uniform stabilizing potential.

The results for other systems are now briefly described. In all cases, the convergence of total energy toward the limiting value is documented by reporting the value of ΔE calculated according to criterion b, as a function of the cutoff radius r ; on the same plot, the absolute value of the leading element of the \mathbf{P} matrix, $p(g) = P_{\text{zazb}}^g$, is also reported. Also note that the inclusion of long-range \mathbf{P} terms does not influence the Coulomb contribution to total energy since the Coulomb integrals associated with \mathbf{P}^g terms decay exponentially with $|g|$.

Hexagonal boron nitride has the same structure as graphite, except for the fact that the two atoms in the unit cell are different. As a consequence, it is a moderately ionic insulator with a fairly large band gap (0.49 au in the present approximation). Figure 3 shows that exchange interactions here are of much shorter range

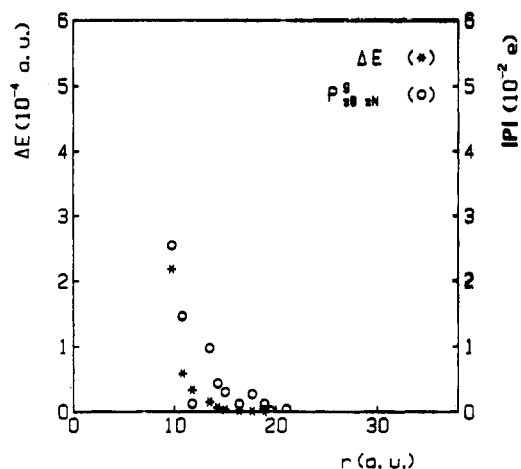


Figure 3. Convergence properties of hexagonal boron nitride: absolute value of the leading \mathbf{P} matrix element, P_{zazb}^g , as a function of the distance r between the involved centers, and corresponding convergence ΔE of total energy toward the limiting value. The scale for energy is on the left, for P on the right of the plot. For other explanations, see text.

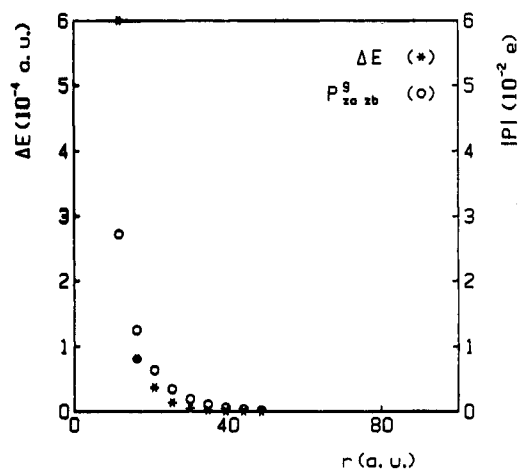


Figure 4. Convergence properties of the alternant structure of *all-trans*-polyacetylene. Symbols as in Figure 3: the leading \mathbf{P} element here is P_{zazb}^g .

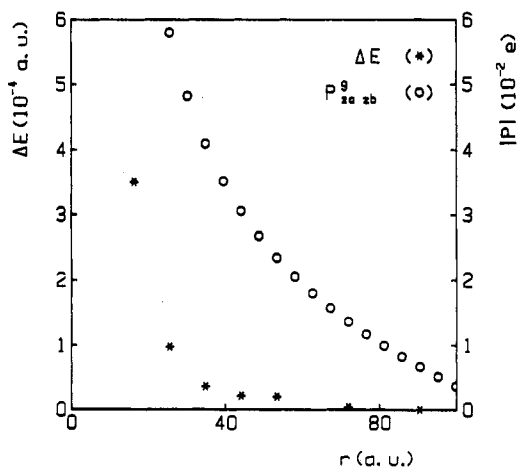


Figure 5. Convergence properties of the symmetric (metallic) structure of *all-trans*-polyacetylene. Symbols as in Figure 4.

than in graphite; the relationship between the results for the two systems is similar to that described in the literature for conducting and nonconducting polymers.

The results for alternant and symmetric polyacetylenes are reported in Figures 4 and 5 and are in close agreement with those discussed in the literature for this type of systems.²⁻⁴ In particular, for the alternant nonconducting case, the decay constant α of $p(g) = P_{\text{zazb}}^g$ [$\alpha = p(g)/p(g-1)$] is found to have a value of 0.57 in good

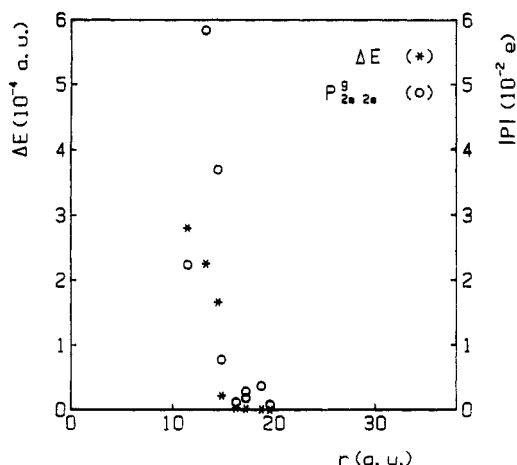


Figure 6. Convergence properties of lithium. Symbols as in Figure 3: the leading P element is here $P_{2s,2s}^g$.

TABLE II: Convergence of Total (E) and Kinetic (K) Energy of Silicon with Respect to the R^{ex} Parameter^a

R^{ex}	N^{ex}	K	E	ΔE^b
4.5	0.3	539.114 223	-555.437 783	1.0 (-1)
8.5	1.8	539.062 776	-555.335 136	8.9 (-4)
11.2	3.1	539.061 613	-555.335 822	2.0 (-4)
13.3	5.9	539.061 262	-555.335 731	3.0 (-4)
15.1	8.0	539.061 571	-555.335 937	8.9 (-5)
16.8	9.8	539.061 566	-555.335 972	5.4 (-5)
18.3	12.2	539.061 555	-555.336 026	

^a N^{ex} is the number of bielectronic exchange integrals in millions; ΔE is the energy difference with respect to the last line energy. Energies and distances in au. ^b x (- y) stands for $x \times 10^{-y}$.

agreement with the value $\alpha = 0.60$ obtained according to the semiempirical formula $\alpha = W/(W + G)$ suggested by Monkhorst and Kertész² and used by Surjan et al.³ (W is the bandwidth and G the gap between valence and conduction bands). With respect to graphite, the conducting polymer has P elements of much longer range (note that the scale of distances is here expanded by a factor of about 2), yet total energy converges at about the same speed; this is simply due to the different dimensionality of the two systems, which reduces by a factor $1/r$ the importance of contributions at a distance r in polyacetylene with respect to graphite.

Lithium (see Figure 6) has been chosen as a simple test system for three-dimensional conductors. At short distances the parallel drop of $|P|$ and ΔE as a function of R^{ex} is more abrupt than in previous cases; at about 15 au the two curves become smoother.

Because of computational limits we were not able to go beyond 20 au (500 unit cells included in the calculation); in the 15–20-au range the ideal r^{-3} behavior (see Introduction) is not evident, possibly because it is disguised by the oscillatory component. It must be noticed that the contribution to total energy from this zone is quite small, of the order of 10^{-5} – 10^{-6} au/cell. Results obtained for metallic aluminum are similar, although the long-range behavior of $|P|$ and ΔE is much smoother than in lithium; in this case contributions to total energy from terms involving distances larger than 15 au are always smaller than 10^{-4} au/cell.

As a second example of three-dimensional systems, silicon was considered (see Table II). Results are relatively similar to those for BN; however, to get a convergence of the order of 10^{-4} au/cell larger distances must be included, similar to the ones found for lithium and aluminum. Finally, in the case of a fully ionic system like MgO, total energy was found to be stable to within 10^{-6} au at $R^{\text{ex}} = 13$ au.

IV. Discussion

The results just presented indicate that the treatment of exchange contributions in crystals does not entail particularly subtle problems, in the sense that convergence of total energy with increasing cutoff radius is quite regular. For insulators the convergence of the exchange series is rapid, and the simple truncation scheme discussed in section II (overlap truncation for the m sum; distance only cutoff for the g and l sums) is economical, sufficiently efficient, and easy to implement. The data presented in the previous section indicate that for alternant polyacetylene, silicon, and BN cutoff radii of 20, 15, and 10 au, respectively, are sufficient to reduce the error in total energy to less than 1×10^{-4} au per cell. The cost to accuracy ratio, evaluated in terms of bielectronic exchange integrals and of total energy, is for those systems roughly the same as we have for the Coulomb series treated with the multipolar expansion technique described in ref 13.

In the case of metals or of zero gap semiconductors things are different; when a distance only criterion with $R^{\text{ex}} = 10$ –15 au is adopted, total energy errors are of the order of $(1\text{--}5) \times 10^{-3}$ au per cell; if higher precision is required, exchange interactions must be taken into account up to fairly large distances. Computational problems may then arise, essentially due to the fact that the number of exchange two-electron integrals increases rapidly with the cutoff radius. Consider for instance the simple case of the graphite monolayer treated with the minimal basis set previously described. If the cutoff radius for all exchange terms is located at 10, 20, and 30 au, the corresponding number of two-electron exchange integrals are 0.74, 2.69, and 6.08 millions, respectively, even if full advantage is taken of point symmetry.¹⁹ If an extended

TABLE III: Performance of the Bipolar Expansion Technique for the Evaluation of Two-Electron Integrals ($\mu \nu | \lambda \sigma$)^a

r , au	L	case a			case b		
		σ	δ_{max}	$ J $	σ	δ_{max}	$ J $
5	0	8.7 (-3)	3.7 (-1)		1.4 (-3)	5.6 (-3)	
	2	8.3 (-4)	3.9 (-3)	1.5 (-2)	9.9 (-5)	3.7 (-4)	4.3 (-3)
	4	3.8 (-5)	3.8 (-4)		7.4 (-6)	4.8 (-5)	
10	0	2.1 (-3)	8.6 (-3)		3.3 (-4)	1.2 (-3)	
	2	5.1 (-5)	2.6 (-4)	6.8 (-3)	6.2 (-6)	2.3 (-5)	2.2 (-3)
	4	7.1 (-12)	5.4 (-11)		4.2 (-8)	3.4 (-7)	
20	0	5.2 (-4)	2.1 (-3)		8.2 (-5)	2.9 (-4)	
	2	3.2 (-6)	1.6 (-5)	3.2 (-3)	3.9 (-7)	1.4 (-6)	1.0 (-3)
	4	3.6 (-12)	2.7 (-11)		6.4 (-10)	5.1 (-9)	
30	0	2.3 (-4)	5.2 (-4)		3.6 (-5)	1.3 (-4)	
	2	6.3 (-7)	1.0 (-6)	2.1 (-3)	7.6 (-8)	2.8 (-7)	7.0 (-4)
	4	2.4 (-12)	1.4 (-11)		5.6 (-11)	4.4 (-10)	

^a $\mu, \nu, \lambda, \sigma$ are STO-2G valence orbitals of carbon,¹⁴ centered at M, N, L, S, respectively. Two cases are considered: Case (a) M coincides with N and L with S; r is the distance between M and L. Case (b) The four centers are distinct and coplanar; the segments NM and LS are 2.674 au long (the bond distance in graphite: their midpoints are at a distance r ; they form an angle of 60° with the line through their midpoints and with each other. L is the level of truncation of the multipolar expansion: charges only ($L = 0$), up to quadrupoles ($L = 2$), up to hexadecapoles ($L = 4$). In each case the 256 two-electron integrals involving the four valence AO's on each center are evaluated exactly (J_i) or approximately (J_i'). $\sigma = [\sum_i (J_i - J_i')^2 / 256]^{1/2}$ is the root-mean-square deviation between the two determinations. δ_{max} is the maximum observed difference $|J_i - J_i'|$; $|J| = \sum_i |J_i| / 256$ is the average absolute value of the integrals. The notation $x.y$ (- z) stands for $x.y \times 10^{-z}$.

STO 3/2-1G basis set is used for carbon (that is, three contracted Gaussians are used for 1s core electrons, while the AO's of the valence shell are described by using two independent functions, one comprising two contracted Gaussians, the other and more diffuse one consisting of a single Gaussian with exponent of 0.2 au,²⁰) these figures increase to 8.3, 31.8, and 80.4 millions, respectively. The situation is obviously even worse for three-dimensional periodic systems treated with extended basis sets.

There are however some features of the exchange series that allow us to drastically reduce the computational burden:

(a) For $R > 10$ au, the near totality of the two-electron exchange integrals describes the interaction between two charge distributions, $\rho(\mathbf{r}) = \chi_1(\mathbf{r}_1) \chi_3(\mathbf{r}_1)$ and $\rho'(\mathbf{r}_2) = \chi_2^*(\mathbf{r}_2) \chi_4^{m+1}(\mathbf{r}_2)$, that are far apart from each other (see eq 1). In such cases, the integral can be evaluated by first effecting a truncated multipolar expansion of the two distributions about the respective center and then considering the interaction between the two sets of multipoles. The accuracy of this technique is documented in Table III with reference to integrals involved in computations for graphite. The bipolar expansion can be truncated at different L values, according to the total amount of charge $S1 + S2$ ($S1 = \int \rho_1(\mathbf{r}) d\mathbf{r}$) involved in the interaction and to the distance between the two centers of expansion. Adopting this procedure is computationally very convenient because the set of multipoles of all relevant product distributions $\chi_1^0 \chi_3^m$ can be evaluated once and for all, and used for both ρ and ρ' because of translational invariance. The corresponding saving factor in computer time is of the order of 5.

(b) Long-range exchange terms may affect to some extent total energy, but leave the wave function essentially unaltered. As shown by Figure 2 for graphite, at 10 au the kinetic energy error is 5–10 times smaller than the total energy one; at 20 au $\Delta E'$ practically coincides with ΔE , confirming that from this distance on the exchange contributions do not affect the \mathbf{P} matrix. This behavior, which is common to all systems investigated here, indicates an economical way for taking into account long-range exchange interactions: the self-consistent calculation is performed

with reference to a small exchange radius, so that there are comparatively few exchange integrals to be manipulated in this computational stage; the neglected terms are then included in the final evaluation of the energy, taking into account only those for which the density matrix results to be nonnegligible. In conclusion, the exchange problem in HF calculations for crystals is not critical, as far as the evaluation of total energy is concerned, if an accuracy of 10^{-4} au is deemed acceptable. In this respect, it would appear not necessary to introduce "mixed" schemes, as recently proposed by different groups.^{1,21} Those authors suggest calculating the \mathbf{P} density matrix with a local density approximation, and use it a posteriori for calculating the correct HF exchange energy. However, while long-range exchange interactions do not affect the wave function, the same is not true for short-range ones. A treatment that takes self-consistently into account the nonlocal nature of the exchange interaction is therefore more reliable, and is in fact feasible even for periodic systems with relatively complex unit cells.

The above analysis has been carried out with reference to systems treated with minimal basis sets; these conclusion should be applicable in general, at least as far as total energy is concerned. When, however, extended basis sets are considered, more severe conditions must be adopted in the treatment of the exchange series, so as to involve terms which are not important for total energy, but are necessary for a precise evaluation of the exchange potential. Otherwise, due to the large variational freedom, instabilities can set in during the SCF process, which may eventually lead to numerical catastrophes.

This topic will be discussed extensively in future work.

Acknowledgment. The computations presented here were effected through funds kindly provided by the Consorzio per il Sistema Informativo CSI Piemonte. Financial support by the Italian Consiglio Nazionale delle Ricerche is also gratefully acknowledged.

Registry No. Li, 7439-93-2; Si, 7440-21-3; graphite, 7782-42-5; boron nitride, 10043-11-5; *trans*-polyacetylene, 25768-71-2.

(19) Dovesi, R. *Int. J. Quantum Chem.* **1986**, *29*, 1755.

(20) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(21) Svane, A.; Andersen, O. K. *Phys. Rev. B* **1986**, *34*, 5512.